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A review on the microwave-assisted pyrolysis technique

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Pyrolysis is a promising bioconversion technique for energy recovery, waste management, and converting biomass into useful energy products which has attracted considerable attention during the past decades. Char/carbonaceous residue, bio-oil, and syngas are the three main products of the pyrolysis process. The pyrolysis technique is one of the major barriers for large-scale commercialization of this method. This study strives to extensively review the recent work on microwave-assisted technology applied to the pyrolysis process as a way of cost reduction. The fundamentals of microwave irradiation and a brief background of pyrolysis are presented. Additionally, biomass resources which can be the raw material for pyrolysis process have been categorized and reviewed in this paper. The effectual parameters of the microwave-assisted pyrolysis process and advantages of this technique have been summarized. It is concluded that microwave-assisted technology is an effectual method to reduce the pyrolysis reaction time and increases the quality of value-added products from different kinds of feedstocks. In addition, this technique can overcome the needs of feedstock shredding and improves the quality of heating as well. Therefore, it can be a suitable method for decreasing the pyrolysis processing cost and a pathway out of poverty for developing countries.

Contents

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Nomenclature

CCD	central composite design
CHP	combined heat and power
CNT	carbon nanotube
DDGS	distillers dried grain with soluble
EF	electric furnace
EFB	empty fruit bunch
FCC	Federal Communications Commission
GDP	growth domestic product
IL-B	1-butyl-3-methylimidazolium tetrafluoroborate
IL-C	1-butyl-3-methylimidazolium chloride
ISM	industrial, scientific, and medical
L	liter
MA	microwave absorber
min	minutes
MSW	municipal solid waste
MW	microwave oven
OECD	Organization for Economic Co-operation and Development
OPF	oil palm fibers
OPS	oil palm shell
PAH	polycyclic aromatic hydrocarbon
PC	personal computer
RSM	response surface methodology
vol%	volume percentage
wt%	weight percentage
W	Watts

1. Introduction

1.1. Classification, production, and consumption of energy resources in the world

Energy is the most important necessity of humans existence on the earth. It is involved in most economic sectors, such as transportation, agriculture, industry and electricity generation, as well as food [1,2]. Generally, there are three main categories of energy resources: fossil fuels, nuclear resources, and renewable resources [3]. There are several factors such as population growth and economic growth which affect the quality and quantity of energy use in the world. Recently, the world's population has been increasing at an enormous rate. Although the growth rate for some nations is negative, the total world population is forecasted to increase by an average rate of 0.9% per year from 6.7 billion in 2008 to 8.5 billion in 2035, as illustrated in Table 1 [4]. Growth domestic product (GDP) affects the amount and type of energy use; the statistics show that GDP growth increases the demand for energy. The real GDP increased at an average rate of 2.4% annually from 2009 to 2011 [5]. Consequently, the total consumption and production of major sources of energy in the world such as liquid fuels, natural gas, and coal have increased in the past decades [6,7]. On the other hand, fossil fuel consumption is known as the main reason for global warming and climate change. Carbon intensity of energy supplies and energy intensity of economic activities, which are the main factors that influence the carbon dioxide emission levels, are increasing day by day [8,9]. The limited supply of fossil-based resources, yearly increases in the price of fossil fuels, increasing demand for energy due to rises in the population growth rate and GDP, and finally climate change, global warming, and the growing rate of carbon emission have stimulated interest in finding new alternative and cheaper energy resources. These alternative energy resources comprise renewable sources, such as geothermal energy [10], solar power [11], wind [12], hydropower [13], and biomass [14,15].

1.2. Renewable energies

Renewable technologies are considered clean sources of energy derived from natural processes and the optimal use of these resources minimizes environmental impacts and produces minimum secondary wastes; thus they are sustainable resources based on current and future economic and societal needs [16]. The limited supply of petroleum resources, global warming issues, increasing greenhouse gas emissions and increasing yearly prices of petroleum based fuels have motivated scientists to find new alternative and cheap energy resources [17]. One of the main strategies to decrease fossil fuel dependence is based on reducing energy consumption by applying energy saving programs focused on energy demand reduction, as well as using renewable energy sources, not only for large-scale energy production, but also for stand-alone systems as replacements for petroleum based fuels. Therefore, the use of renewable energies in the world will increase in order to have a more sustainable energy mix, reduce greenhouse gas emissions and a lower dependency from fossil fuels [18,19].

About 14% of the total world energy demand is supplied by renewable energy sources, meaning that they still represent a small part of today's global energy picture. Renewable energy resources include biomass, hydropower, geothermal, solar, wind and marine energies [16,20–22]. Forest origins and wastes, agricultural crops and residues, and animal wastes are some potential natural energy sources of biomass. Three different phases of fuels can be produced from biomass: liquid-based, solid-based, and gas-based [23–26]. Geothermal resources have been used to generate

Table 1
Biomass resources classification.

Biomass resources		
Virgin resources	Forest resources	Any type of wood like pine beetle wood, or new types of woody and forest biomass such as willow, hybrid poplar, balsam poplar, aspen
	Oil/crops	Wheat, barley, tame hay, corn, canola, palm oil, soybean, flax, oat, straw, pasture grasses
Residues	Wood residues	Bark, branches, leftover treetop, and leaves from harvest and thinning operations or left over from felling, sawdust, shavings from pulp mills and saw mills
	Agricultural residues and wastes	Residual fraction of primary crop (wheat, barley, tame hay, oat, etc.) harvest, waste oil/fat
	Livestock residues	Readily available source of waste biomass like livestock excrement and livestock carcass
Municipal solid waste (MSW)	Residential Non-residential	Newsprint, cardboard and boxboard, mixed paper, glass, ferrous metals, copper and aluminum, mixed metals, white goods, electronics, plastics, tires, construction, renovation and demolition, organics, other materials

power in many countries around the world; some of these works related to geothermal power generations are discussed elsewhere [27–32]. Solar energy has been utilized by many countries and has become more popular as a valuable energy source. It is one of the most important renewable resources with a high potential for solving the energy crisis in the world [33–35]. Wind energy is one of the greenest renewable resources for electricity generation, via mechanical power in windmills, and pumping water in wind pumps, and also sailing ships; in addition, it does not generate pollution or greenhouse gases [18,36,37].

2. Biomass

2.1. Biomass resources

Biomass is known as living or recently living biological materials which can be used as a source of energy and seems to have a high potential for use as an energy source [38,39]. Goran et al. believed that biomass has the potential to even be one of the main global primary energy sources during the next century [40]. It is one of the most promising alternative sources which can alleviate the energy crisis, reduce pollution and global warming, and it can contribute to sustainable development [16,41]. These resources are renewable, carbon-neutral, have considerably lower sulfur contents, and are plentiful in amount on earth, and can be the best alternative to fossil fuel resources [42]. Biomass can be used directly to produce energy e.g. dead trees/wood, or can be converted into any other type of value-added product such as biodiesel, bio-fuel, etc. [2,43,44]. The production of electricity and heat using biomass is developing in many European countries such as Austria, Finland, Germany, and the UK, to name a few. Some other countries (Sweden, Denmark, the US, and several other OECD countries) are also investing in this area. Sweden supplies more than 50% of the country's heating needs using biomass [45]. Agricultural wastes, such as rice or coconut husks, have been used in developing countries for small-scale power and heat production [46], while countries with large sugar industries, such as Brazil, Columbia, Cuba, India, the Philippines and Thailand, use sugar cane wastes as a heat and power source [47].

Therefore, for sustainable developments in the coming future, it is essential to utilize biomass resources efficiently. The first step for the development of these resources is to categorize them. As illustrated in Table 1, biomass resources are divided into three major categories: virgin resources, residues, and municipal solid waste. All of these can be promising sources of energy production for the future using suitable conversion processes. Specially, the forest and agricultural residues, municipal solid wastes, and other kinds of wastes are promising alternatives for microwave pyrolysis processes.

Lignocellulosic feedstocks including virgin resources and residues such as wood [48], coffee hulls [49], rice straw [50,51], waste tea [52], and wheat straw [53,54] showed high potentials as the raw materials for the pyrolysis process. Sewage sludge [55–57] and automotive industry wastes including auto shredder residues [58] (which contains plastic, wood, fibre, glass, textiles, and metal etc.) are other potential options for the pyrolysis process.

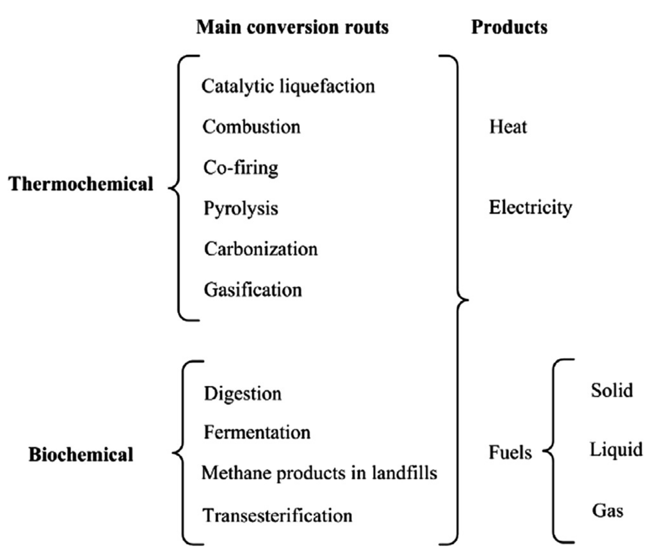


Fig. 1. Major conversion technologies for converting biomass into useful energy carriers [60].

2.2. Biomass conversion technologies

Bioenergy conversion technologies are used to convert biomass into useful energy. These technologies are mainly divided into two categories: thermochemical and biochemical conversion. In thermochemical conversion pathways, heat and chemical catalysts are used for the production of energy from biomass, while biochemical conversion pathways use biological organisms and biological catalysts for transforming biomass into energy and value-added products. A wide range of useful energy products can be obtained from biomass using these conversion technologies, including different types of fuels, heat, and power [59]. Fig. 1 illustrates the main conversion technologies which have been used or are under development for the production of secondary energy carriers. Combustion (domestic heating, combined heat and power (CHP), and co-combustion), gasification (large-scale and small-scale), and pyrolysis are known as the main thermochemical

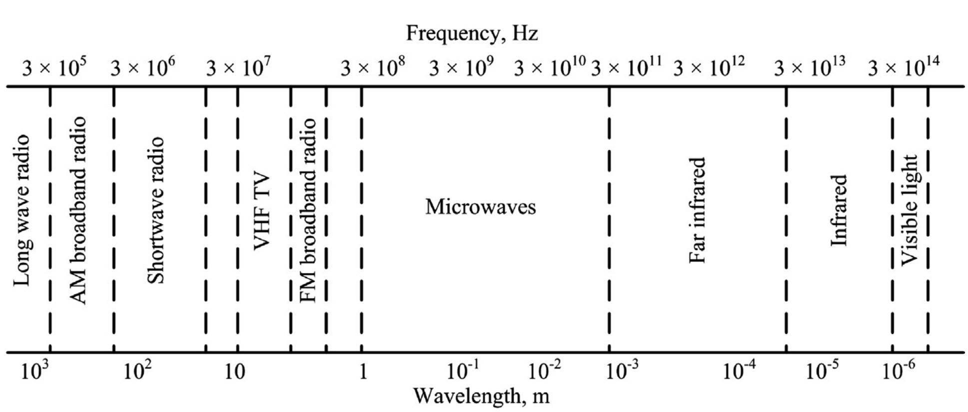


Fig. 2. The electromagnetic spectrum.

conversion pathways, while fermentation and trans-esterification are the most common biochemical conversion pathways for ethanol and biodiesel production [59,60].

3. Microwave heating technology

3.1. Fundamentals of microwave heating

Von Hippel formulated the basic understanding of macroscopic microwave interactions with matter for the first time [61]. The application of microwave technology in the thermal treatment of biomass has increased from the mid-nineties. This technique not only reduces the energy consumption and processing time, but also enables the use of new chemistry (unique internal heating phenomenon associated with microwave energy). It can also enhance the overall production quality [62,63].

Microwave irradiation is an electromagnetic irradiation in the range of wavelengths from 0.01 m to 1 m and the corresponding frequency range of 0.3–300 GHz. Generally, radar transmissions use the wavelengths between 0.01 m and 0.25 m and telecommunications use the remaining wavelengths [64]. Most microwave reactors for chemical synthesis and all domestic microwave ovens operate at 2.45 GHz frequency, which corresponds to a wavelength of 12.25 cm. However, 915 MHz and 2450 MHz are two frequencies which are reserved by the Federal Communications Commission (FCC) for industrial, scientific, and medical (ISM) purposes [65,66]. This is in order to avoid any interference with telecommunications and cellular phone frequencies [67]. The microwave region of the electromagnetic spectrum is shown in Fig. 2. As indicated in this figure, this region lies between the infrared and radio frequencies [68].

Microwaves are normally defined as the electromagnetic waves which consist of two perpendicular components, namely electric and magnetic fields, as shown in Fig. 3. According to the interaction of microwave irradiation (electric component of microwave field) with materials, there are three ways in which a material may be categorized: (1) insulator or microwave-transparent material where microwaves pass through without any losses (e.g. quartz, teflon, etc.), (2) conductor where the microwaves cannot penetrate and are reflected (e.g. metals), and (3) absorber where the microwaves can be absorbed by the material (e.g. water, oils, etc.). Microwave dielectrics are known as a material which absorbs microwave irradiation, thus microwave heating is called dielectric heating [69].

3.2. Conventional heating versus microwave heating

Conventional thermal heating is known as a traditional heating system (with an external heat source such as an oil bath or heating mantle) where heat is transferred from the surface towards the center of the material by conduction, convection, and radiation. This heating system is relatively slow and inefficient and depends on the thermal conductivity of the material and convection

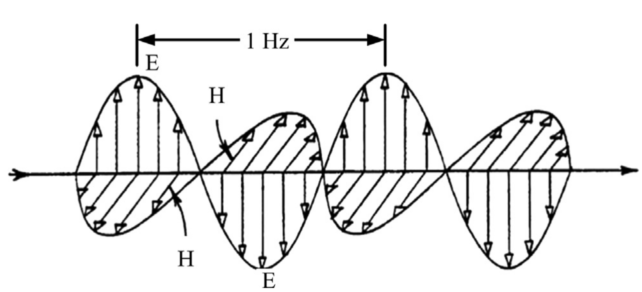


Fig. 3. Electric (E) and magnetic (H) field components in microwaves.

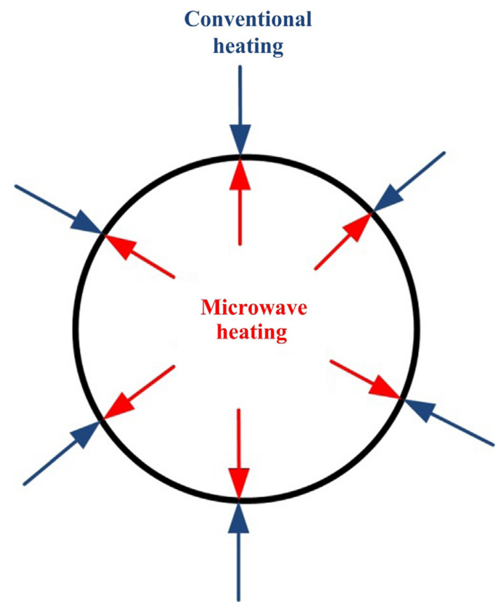


Fig. 4. Microwave and conventional heating nature.

currents. On the contrary, dielectric heating transfers electromagnetic energy to thermal energy; it is a kind of energy conversion rather than heating. The microwaves can penetrate materials and deposit energy, thus the heat can be produced throughout the volume of the materials rather than an external source (in core volumetric heating). Fig. 4 demonstrates the difference in mechanism for conventional and dielectric heating systems. As illustrated in this figure, the center of the material is at a higher temperature than the surrounding material in microwave heating, unlike conventional heating [65,69]. According to the literature, there are three possible ways (combination of two or all three contributions) of chemical reaction enhancement using microwave irradiation technique [70], including (i) thermal effects (the influence of a high reaction temperature which can be rapidly attained when irradiating polar materials in a microwave field) [71], (ii) specific microwave effects (can be caused by the unique nature of the microwave irradiation heating mechanism in a microwave field and cannot be achieved by conventional heating) [72], and (iii) non-thermal effects (chemical transformation accelerations that cannot be defined in terms of thermal or specific microwave effects) [73].

4. Pyrolysis process

4.1. General overview and principles of pyrolysis process

It is essential to select the appropriate technology for the conversion of potential biomass resources into value-added products in order to moderate the energy crises and their consequent environmental degradation. Combustion or incineration (complete oxidation), gasification (partial oxidation), and pyrolysis (thermal degradation in the absence of oxygen) are the three main thermochemical conversion routes for the conversion of biomass resources into heat, electricity, fuels, chemicals, or any other value-added products [74,75].

Pyrolysis is the thermo-chemical decomposition of hydrocarbon (or organic) materials at elevated temperatures in the absence of oxygen. It offers the potential for greater efficiencies and less pollution for the production of reactive intermediate products from biomass in comparison with other techniques. There are many effectual factors in the pyrolysis process, such as biomass

(raw material) composition and experimental conditions [76]. Pyrolysis mainly consists of two main stages known as primary and secondary pyrolysis [77]. Primary pyrolysis covers devolatilization (dehydration, dehydrogenation, and decarboxylation) of the main constitutes, while secondary pyrolysis involves the thermal or catalytic cracking of heavy compounds or char into gases such as CO, CO_2, CH_4, and H_2 [78].

4.2. Pyrolysis conditions

Reaction conditions are significant factors which influence the yield and properties of the final products. Pyrolysis process can be divided into three categories namely slow, fast, and flash pyrolysis, depending on the reaction rate, residence time, and heating rate, as shown in Table 2 [79]. The main product of slow pyrolysis is solid char [80], while the main products of fast and flash pyrolysis are liquid fuels [81,82]. Previous studies showed that the char yield decreases when the reaction temperature increases [49]; while a longer residence time increases the char yield because of an increasing secondary reaction [83]. In addition, higher heating rates favor the production of liquid and gaseous fractions [84] and the liquid fuel yield maximizes at intermediate temperature ranges.

4.3. Pyrolysis products

Pyrolysis of biomass is a complicated process which can provide three different products in the three different phases of solid, liquid, and gas depending on the feedstock characteristics and pyrolysis reaction conditions, as illustrated in Fig. 5 [85].

The solid fraction or pyrolysis char is a carbonaceous residue produced in the primary and secondary pyrolysis reactions [77]. It can be used as (1) a solid fuel for the production of heat and electricity, (2) feedstock for gasification processes, and (3) feedstock for activated carbon production, (4) feedstock for carbon nanofilaments production, among other uses. Biochar is another solid fraction co-product which has several applications such as (1) soil quality enhancement, (2) carbon sequestration for global climate change mitigation, (3) soil water improvement, (4) nutrient retention, (5) soil erosion, and (6) water contamination reduction, etc. [86–88].

The liquid or oil fraction is another product of biomass pyrolysis which can be a promising alternative energy source for fuel oil or diesel. The produced oil needs to be upgraded by residue removal and lowering the oxygen content [89]. As it can be stored and transported, there is no need use the oil at the production site. The main industrial uses of pyrolysis oil can be summarized as follows: (1) combustion fuel for heat generation [90]; (2) power generation [91]; (3) transportation fuel [92,93]; (4) wood flavors, wood preservatives, and liquid smoke [94]; (5) chemical and resin production [95]; (6) used in making adhesives [96].

The gas produced during the pyrolysis process (light molecular weight gases) is another valuable byproduct. A vast diversity of biomass materials can be converted to combustible gases (H_2, CO, C_2H_2, CH_4, C_2H_4, etc.). Basically, increasing the reaction temperature in pyrolysis creates a significant increase in gaseous product yield due to thermal cracking of heavy compounds [97]. In addition, higher heating rates increase the volatile (liquid and gas fraction) yield [84]. These combustible gases can be used as the direct firing in boilers for heat production or in gas turbines or engines for electricity production.

Table 2
Pyrolysis classification [79].

Pyrolysis technology	Residence time (s)	Heating rate (K/s)	Temperature (K)
Slow	450–550	0.1–1	550–950
Fast	0.5–10	10–200	850–1250
Flash	< 0.5	> 1000	1050–1300

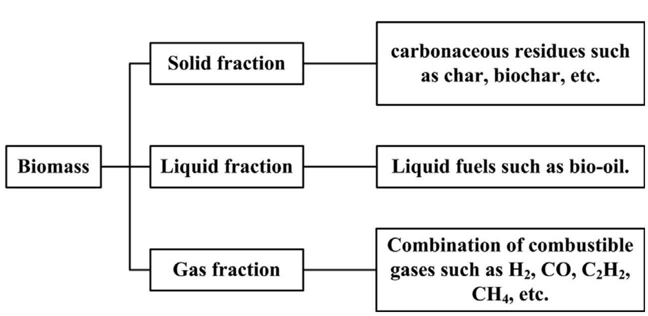


Fig. 5. Pyrolysis products [85].

4.4. Microwave-assisted pyrolysis technique

The microwave technique is one of the most promising methods of enhancing and accelerating chemical reactions, as discussed in previous sections. The reactions can be completed more efficiently in comparison with other conventional methods due to effective heat transfer profiles [98]. This is emerging as one of the best technologies in the pyrolysis process; it reduces residence time and accelerates chemical reactions, which leads to energy saving. In this section the microwave-assisted pyrolysis method has been reviewed extensively.

Zhao et al. [99] reported the effect of temperature on the microwave-induced pyrolysis of biomass (wheat straw). A 3000 W, 2.45 GHz domestic microwave oven was modified to perform the experiments. The microwave reactor was equipped with a two-figure electronic balance to measure the weight, a thermocouple for reading the pyrolysis temperature, an electric heating device to circulate the air in the reactor for preventing the condensation of liquid phase products on the quartz reactor wall and pipelines, and a temperature control function to produce constant temperatures during the microwave pyrolysis reaction. For each batch, 5–30 g of wheat straw was placed in the reactor in the presence of a constant N_2 flow (3 L/min) as the carrier gas. It was observed that the temperature is an effectual parameter in the performance of microwave pyrolysis process. Increasing the temperature from 400 °C to 600 °C caused an increase in the yield of gas products and the ratio of combustible gas to total gas products from 17.69 wt% to 22.27 wt%, and from 67.21 vol% to 77.14 vol%, respectively. Increasing the temperature from 400 °C to 600 °C escalated the specific surface area of the solid fraction from 0.89 m^2/g to 9.81 m^2/g and the pore volume from 0.006 cm^3/g to 0.012 cm^3/g, while decreasing the average pore size from 282.16 nm to 46.64 nm, respectively.

Hu et al. [100] studied the effect of microwave power level and catalysts such as activated carbon, CaO, SiC and solid residue on the products of microwave-assisted pyrolysis of *Chlorella vulgaris*. A 3750 W, 2.45 GHz microwave was used to perform the experiment which was manufactured by Guangzhou Wancheng Microwave Equipement Co. Ltd. A 500 mL three-neck quartz reactor was placed in the microwave oven; this reactor was connected to a nitrogen tank and the N_2 was applied as the carrier gas with a 300 mL/min flow rate. From the middle neck a thermocouple was inserted to measure the temperature; and the last neck was used to transfer the condensable and non-condensable gases to the collecting bottles. It was observed that increasing the microwave power level from 750 W to 2250 W increased the temperature level from less than 200 °C to nearly 800 °C, improved the gas

product yield, and decreased the solid fraction yield. The results indicated that the maximum yield of bio-oil (35.83 wt%) was obtained under 1500 W microwave exit power, while the maximum gas yield (52.37 wt%) was gained using 2250 W microwave exit power. It was concluded that increasing the microwave power level and catalyst concentration ameliorated the gas production, and that solid residue results were the best after activated carbon was used among the catalysts. The maximum yield of bio-fuel (87.47%) was obtained by using the optimal content of activated carbon (5%); it also increased the gas yield of *C. vulgaris* by 75.66%.

The effects of reaction time and temperature on the yield of syngas, bio-oil, and charcoal from Douglas fir sawdust pellet using a microwave pyrolysis method were reported by Ren et al. [101]. Central composite design (CCD) and response surface analysis were used to optimize the production of volatiles and charcoal. A 1000 W batch microwave oven (Sineo MAS-II) was used at 700 W to carry out the experiments. In each batch, 400 g of Douglas fir sawdust pellets was placed in a 1 L quartz reactor inside the microwave oven. It was found that increasing the reaction time and temperature increased the yield of volatiles (including both bio-oil and syngas); additionally, the highest yields for bio-oil and syngas were obtained at 471 °C after 15 min. The yield of volatiles (depending on pyrolysis condition) and bio-oil (based on dry biomass basis) ranged from 39.3 wt% to 68.8 wt% and 33.8 wt% to 57.8 wt%, respectively. Besides, the charcoal and syngas yields were ranged from 31.2 wt% to 60.7 wt% and 7.9 wt% to 15.0 wt% depending on the reaction conditions.

The catalytic effects of eight different inorganic additives on pyrolysis of pine wood sawdust were investigated by Chen et al. [102]. The experiments were carried out using NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4, $Fe_2(SO_4)_3$ as the additives and SiC as the absorber under microwave irradiation at 470 °C. N_2 with a flow rate of 0.2 m^3/h was used for 15 min in order to expel the air from the reactor. It was determined that the yield of solid portion increased by applying each of the eight additives, while the yield of gaseous products decreased and the liquid product yield did not show a dramatic change. H_2, CH_4, CO, and CO_2 were the gases produced from pyrolysis using all of the eight additives, and the sodium additives were found to be the most effective. The amount of CO_2 and CH_4 decreased when using any of these additives, while all of them increased the amount of H_2 except NaCl, TiO_2, and $Fe_2(SO_4)_3$. In addition, the amount of CO decreased when using any of the additives except HZSM-5 and Na_2SiO_3. All of the alkaline sodium compounds ameliorated the acetol formation and their increasing effect followed the order of $NaOH > Na_2CO_3 \approx Na_2SiO_3 > NaCl$, while HZSM-5 had no significant effect on acetol formation and TiO_2 decreased the acetol formation.

Omar et al. [103] investigated the characterization of oil palm empty fruit bunch (EFB) for pyrolysis using the microwave irradiation method. As water is a good microwave absorber, the results indicated that the high water content of EFB improved the microwave heating by fast drying, and that a potassium content of 12.8% influenced the microwave absorption positively as well. In addition, high volatile content (70%) is a significant advantage of high reactivity. The dielectric properties and moisture content were observed to be proportional up to 60% at 2.45 GHz. It was concluded that the fuel and chemical properties of EFB are comparable to the other biomass feedstocks, thus it has a high potential to be the raw material for microwave pyrolysis.

Microwave copper interaction was applied to co-pyrolysis of waste polystyrene and Makarwal coal based on high temperature by Hussain et al. [104]. This method increases the co-pyrolysis and gives 18% residues, 6% gases, 10% sulfide-containing aqueous fraction, and 66% oily fraction. It was observed that the amount of oil produced was greater than the aqueous part. The produced compounds were found to be aromatic in nature; oily fraction was tested by GC–MS and it was found to be in a narrow range; residue was obtained as porous and non-porous; and finally the produced gases contained acetylene and sulfur.

Microwave-assisted pyrolysis was applied to bio-oil production from sewage sludge by Tian et al. [105]. A novel and feasible method was presented in this study to obtain the maximum bio-oil yield. The relationship between mass balance of the products and microwave exit power was developed to find the most efficient range for transforming the sludge into bio-oil. The results revealed that the best range to get the highest bio-oil yield was about 400 W to 600 W. Increasing the range of exit power to 600–800 W caused a favorable improvement in gas yield, but the bio-oil yield was decreased. Furthermore, increasing the power range to above 800 W favored gas formation at the expense of the solid fraction, while the bio-oil yield remained constant. It was found that the maximum bio-oil yield of 49.8% was obtained at 400 W microwave exit power for 6 min with high calorific value of 35.5 MJ/kg and a low density of 929 kg/m^3. By increasing the microwave exit power from 200 W to 1200 W, the solid fraction yield decreased from 77.3 wt% to 32.6 wt% and the bio-gas yield increased from 4.4 wt% to 60.21 wt%, respectively.

The fast pyrolysis of two kinds of biomass (rice straw and sawdust) was studied using the microwave irradiation technique described by Du et al. [106]. The effect of microwave exit power (160 W to 800 W), microwave heating time (up to 25 min), and the catalyst dosage (0.0 to 0.5 catalyst/biomass ratio) were investigated in this study. Two different types of ionic liquids, namely 1-butyl-3-methylimidazolium chloride (IL-C) and 1-butyl-3-methylimidazolium tetrafluoroborate (IL-B), were used as the catalyst. The results indicated that a small amount of bio-oil was produced when the microwave exit power was lower than 480 W, while the produced bio-oil yield from rice straw reached 38% with 640 W microwave exit power and increased to 42% when the ratio of IL-C/rice straw reached 0.15. In addition, 34% bio-oil yields were obtained using 0.40 IL-B/sawdust in 20 min microwave heating. A minimum initiation time of 2 min and 8 min was observed for bio-oil formation when catalyzed by IL-C and IL-B, respectively. It was concluded that the bio-oil yields from rice straw reached a stable value after 20 min microwave irradiation time (for both catalysts).

The application of microwave-assisted pyrolysis of methane on the growth and morphology of carbon nanostructures (carbon nanospheres and CNTs) in the absence of a catalyst was studied by Zeng et al. [107]. A vertical quartz tube was placed in a 2.45 GHz domestic microwave oven to carry out the experiment. A microwave absorber material carbon/carbon composite without mineral content was placed in the tube, which acted like a catalyst for nanostructure growth. Flushing the nitrogen before performing the experiments eliminated the oxygen from the cavity. The reaction was performed in a mixed gas flow CH_4/N_2 (ratio of 1:4) for 60 min and then the substance deposited on the quartz wall was used for further analysis. The results demonstrated that microwave-assisted pyrolysis is a novel and promising approach for synthesizing carbon nanostructures. Besides, the experimental conditions, such as methane to nitrogen ratio, reaction temperature, and total gas flow rate, affected the nature of the produced nanostructures.

Huang et al. [108] studied the production of H_2-rich fuel gas from rice straw using microwave-induced pyrolysis. A 2.45 GHz single-mode microwave with maximum power of 2 kW was used to conduct the experiments. The reaction tube and sample holder, both with quartz quality, were placed in the cavity and nitrogen was used as the carrier gas in the pyrolysis process. H_2 (50.67 vol %), CO_2 (22.56 vol%), CO (16.09 vol%), and CH_4 (7.42 vol%) were the primary gases produced from the process, which means that about 60% of the products can be utilized as bioenergy. It was concluded

that the generated hot-spots by microwave ovens could be effective in H_2 production.

The microwave pyrolysis process was conducted using methane as the carbon source without applying a catalyst to synthesize SiC nanowires on the quartz plate directly by Fu et al. [109]. In this study, the effects of reaction conditions, such as the reaction gas concentration and the reaction temperature, on the morphology of the SiC nanowires were investigated. It was concluded that a high purity nanowire could be synthesized using this novel method.

Microwave technology was used in the pyrolysis and analysis of six different fractions of waste electrical and electronic equipment by Andersson et al. [110]. The raw materials ranged from light dust to particles sized 7–12 mm, with four of these fractions coming from dry separation and the remaining two fractions from wet separation. A lab scale 2.465 GHz microwave pyrolysis reactor equipped with three magnetrons was used to perform the experiments in a power output of 1 kW. This method was found to be successful in upgrading the wastes to higher value materials (oil, gas, and solid residue). It was found that less organic dust materials required shorter times for heating and that particulate materials seemed to have a larger mass reduction due to the larger plastic contents. In addition, the highest mass reduction occurred during the heating phase and started above 100 °C.

Chemat and Poux [111] studied the effect of microwave heating on the pyrolysis of urea into cyanuric acid. It was found that for classical and microwave irradiation heating techniques, there was no non-thermal effect when using homogeneous pyrolysis under the same reaction conditions of pressure, temperature, and concentration. On the other hand, the yield of products increased from 15.2% to 61.2% at 300 °C and from 4.6% to 9.9% at 200 °C by adding graphite (under heterogeneous conditions). In addition, the reaction rates in heterogeneous pyrolysis were significantly increased.

The effects of microwave-induced pyrolysis of two types of biomass, namely oil palm shell (OPS) and oil palm fibers (OPF), in the presence of char obtained from conventional pyrolysis of OPS as the microwave absorber (MA) were studied by Salema and Ani [112]. In this study, the OPS were used without any grinding, while OPF was ground to smaller sizes. A 1 kW, 2.45 GHz domestic microwave oven was modified to perform the experiments. This oven was equipped with a fluidized bed quartz glass reactor, a steel distributor plate, and two k-type metallic thermocouples to record the temperatures on the surface and inside the material. The ratio of OPS/OPF to MA was varied from 1:0.25 to 1:1 at the constant microwave exit power of 450 W and 25 min reaction time to investigate its effect. The results indicate that increasing the biomass to MA ratio from 1:0.25 to 1:0.5 decreases the char production, while increasing the bio-oil and gas production for both OPS and OPF. In addition, increasing the biomass to MA ratio from 1:0.5 to 1:1 increases the char yield and decreases the bio-oil yield, while the gas yield stays relatively constant. In conclusion, the large biomass particle sizes can be used in microwave reactors, resulting in grinding and moisture removal cost savings.

Lei et al. [113] investigated the pyrolysis of distiller′s dried grain with soluble (DDGS) for the production of biochar, bio-oil, and syngas under microwave irradiation. In this research, the effect of critical reaction conditions such as reaction time, temperature, and microwave exit power were studied and analyzed using response surface methodology (RSM). It was observed that the biochar, bio-oil, and syngas recovery were between 22.61–62.2%, 26.5–50.3%, and 9.78–31.52%, respectively, depending on the pyrolysis conditions. In addition, with an increased reaction temperature and time, the bio-oil and syngas yields increased, while the biochar yield decreased. The highest yield of bio-oil (50.30%) was observed at 684 °C, 800 W after 13 min and the highest syngas yield (31.52%) and lowest biochar (22.61%) yield were observed in the same reaction conditions of 650 °C, 18 min, and 900 W. The main conclusions of this study were that reaction time and temperature are the most effective reaction conditions in microwave pyrolysis of DDGS.

Wan et al. [114] evaluated the effect of different catalysts on microwave-assisted pyrolysis of dry corn stover and aspen wood pellets. Different types of acids, salts, and metal oxides, including $K_2Cr_2O_7$, Al_2O_3, KAc, H_3BO_3, Na_2HPO_4, $MgCl_2$, $AlCl_3$, $CoCl_2$, and $ZnCl_2$, were mixed with biomass raw materials (100 g dry biomass mixed with 8 g powders/crystals) before the microwave pyrolysis process. A 2450 MHz, 875 W constant input power microwave reactor was used for around 20 min for each test, with a temperature ranging from 450 °C to 550 °C. Some of these catalysts, such as KAc, Al_2O_3, $MgCl_2$, H_3BO_3, and Na_2HPO_4, increased the bio-oil fraction by reducing the charcoal or gas yield, or both. It was concluded that the catalysts may act as microwave absorbers and speed up the heating rate. $MgCl_2$ was found to be an effectual catalyst on the products of microwave-assisted pyrolysis; the maximum bio-oil yield for dry corn stover (4 g/100 g sample) and aspen wood pellets (8 g/100 g sample) were about $42.70 \pm 1.11\%$ and $41.12 \pm 1.41\%$, respectively. Among the other catalysts, Na_2HPO_4, $K_2Cr_2O_7$, and Al_2O_3 were found to yield the maximum bio-oil ($\approx 44\%$), syngas ($\approx 37\%$), and charcoal ($\approx 30\%$) amounts, respectively.

Microwave-assisted pyrolysis was applied to a wild type algae strain named *Chlorella* sp to investigate the possible bio-oil production from it by Du et al. [115]. A Panasonic microwave oven (NN-SD787S) with a maximum exit power of 1.25 kW and 2.45 GHz frequency was used to perform the pyrolysis process. The sample was located in a 500 mL quartz flask and nitrogen was used as the carrier gas with a flow rate of 500 mL/min in these experiments. In order to enhance the heating quality, char (produced from biomass pyrolysis) was used as the microwave absorber with the lowest effective ratio of 1:5 (char to biomass, gr/gr). The maximum bio-oil yield of 28.6% was obtained at 750 W microwave exit power and by increasing the power the bio-oil yield was decreased. It was found that the gas yield was improved by about 12% when increasing the power from 500 W to 1250 W. The produced bio-oil compounds were comparable to those of fossil fuels such as crude oil, gasoline, and diesel.

Microwave irradiation was introduced as a promising technology for pyrolysis of problematic waste automotive engine oil by Lam et al. [116]. The waste oil was placed in a bell-shaped quartz reactor which was filled with particle carbon and stirred during heating by the microwave oven (5 kW). The heating rate of 60 °C/min was applied to provide a pyrolysis temperature between 250 °C and 700 °C, and nitrogen was applied as the carrier gas with a flow rate of 0.1 L/min to 0.75 L/min. Two thermocouples were used to detect the reaction temperature, one from the bottom of stainless steel stirrer shaft and the other one at the top of the carbon bed. The results indicated that 88 wt% yield of pyrolysis oil can be achieved by using this method at 250 mL/min N_2 rate and 5.0 kg/h waste oil feed rate. The best N_2 purge rate was 250 mL/min and the yield was improved by increasing the waste oil feed rate from 0.4 kg/h to 5.0 kg/h. It was concluded that microwave pyrolysis technology has exceptional promise for recycling wastes such as waste oils.

Microwave pyrolysis was applied by using activated carbon as the catalyst for the production of phenol and phenolics from Douglas fir (lignocellulosic biomass) by Bu et al. [117]. The ratio of activated carbon to biomass was varied from 1.32 to 4.86 and the reaction temperature and reaction time were varied as well, while the microwave input power was fixed at 700 W with a heating rate of 60 K/min. The results showed a high concentration of phenol (38.9%) and phenolics (66.9%) under the following reaction conditions: 3:1 catalyst to biomass ratio; 589 K reaction temperature; 8 min retention

time. The produced phenol can be used as feedstock for bio-based phenols or directly as fuel after upgrading.

Lam et al. [118] discussed the microwave pyrolysis of automotive engine oil to investigate the characteristics of incondensable gases products. The same experimental apparatus used in Ref. [116] were used to perform the tests; the only change was the installation of a membrane filter in order to remove the metallic solid residue in the pyrolyzed volatiles before entering the condensation system. About 41 wt% of gases were recovered with a high concentration of light aliphatic hydrocarbons (up to 86 vol%). The produced gases contained up to 19 vol% H_2 and up to 35 vol% H_2+CO. It was concluded that the use of microwave irradiation with the carbon bed assistance improved the production of valuable gases as an alternative source of hydrogen or hydrocarbon energy from waste oil.

Quan et al. [119] investigated biofuels with high concentrations of phenol and phenolics using the microwave-assisted pyrolysis process. The same microwave design as previously described in Ref. [117] was applied for the pyrolysis process in this study. Activated carbon was used as the catalyst for phenolic-rich pyrolysis oil production. The reaction time, reaction temperature, and catalyst to feedstock ratios were the main variables in this study. The high concentration of phenol (38.9%) and phenolics (66.9%) in the produced bio-fuels, which was due to the effect of activated carbon on the decomposition of lignin, showed that the microwave-assisted pyrolysis technique is a promising method for the bioconversion of Douglas fir (biomass feedstock). The liquid yield ranged between 25% and 38% (wt of feedstock), while it was 45.2% without activated carbon. It was observed that activated carbon significantly increased the volatile yields. Applying higher temperatures increased the gas yield and decreased the solid fraction yield, while the liquid yield increased from 32.3% (589 K or 315.85 °C) to 38.8% (673 K or 399.85 °C), but decreased at higher temperatures. The catalyst to biomass ratio was found to be between 3 and 4 for maximizing the volatile and liquid yields. The optimum reaction time for the maximum yield of volatiles was 12 min, while its effect was not as significant as other variables.

Microwave heating thermal cracking (pyrolysis) of used car engines was discussed by Lam et al. [120]. A quartz reactor containing 1 kg carbon as the receptor was placed in the microwave oven; a 0.2 L/min flow rate was applied to nitrogen as the carrier gas; an agitator with 6 rpm speed was used to stir the materials inside the reactor; and the reaction temperature was varied from 400 °C to 700 °C. The optimum reaction temperature for the greatest yield of commercially-valuable products was 600 °C. At this temperature the liquid yield was nearly 75%, while the gas and solid fraction products were at their minimum values. A significant level of metal contaminants was found in the recovered liquid oils: 46% reduction in Cd; 32% reduction in Cr; and 93–97% reduction in Cu, Ni, Pb, Zn, Fe. The results of this study showed that microwave pyrolysis is a promising method for treating wastes such as engine oils.

Lin et al. [121] developed a pilot scale microwave reactor to produce bio-oil from sewage sludge. In this study, the effect of reaction parameters and chemical additives were investigated on the yield and quality of the bio-oil produced. A 2.45 GHz modified microwave oven made by Qingdao MKW Microwave Applied Technology Co. Ltd, was used in this study. Nitrogen with a flow rate of 5–20 L/min was applied to 3.5 kg dried sewage sludge in each experiment. Five types of additives (KOH, H_2SO_4, H_3BO_3, $ZnCl_2$, and $FeSO_4$) were tested to study their effect on bio-oil composition. It was found that the maximum yield of bio-oil (30.4%) was obtained at 8.8 kW microwave exit power and a final pyrolysis temperature of 500 °C (with a range of 200–400 °C pyrolysis temperatures). All types of catalysts decreased the bio-oil yield, while KOH, H_2SO_4, H_3BO_3, and $FeSO_4$ improved the bio-oil quality according to calorific value, density, viscosity, and carbon content. In contrast, $ZnCl_2$ had negative effects on the product's quality. KOH favored the alkane and monoaromatic contents, while H_2SO_4 and H_3BO_3 increased the formation of cyclics, ketones, alcohols, and nitriles and decreased the formation of amides and esters. The results of this study indicated that microwave pyrolysis is an industrially feasible method for sewage sludge conversion to bio-oil.

The source and energy recovery of rice straw using microwave induced pyrolysis was discussed by Huang et al. [122]. A single-mode microwave oven (with 2 kW maximum power and 2.45 GHz frequency) equipped with a thermocouple sensor at the bottom of the sample was used for this pyrolysis process. Microwave exit power and particle size were two key parameters influencing the pyrolysis performance. The results indicated that when the size of the particles is small, the lower microwave power will be satisfactory for pyrolysis of rice straw. The resulting solid fraction analysis (specific surface area, seta potential, and Cu^{2+} adsorption) showed a high potential in the water and waste water treatment (removal of metallic contaminants). Rich flue gas was another product of this process (about half of the rice straw sample) with H_2 (55 vol%), CO_2 (17 vol%), CO (13 vol%), and CH_4 (10 vol%). In conclusion, the authors stated that the total biomass recovery by using the microwave-assisted pyrolysis method was no longer a fantasy and it is now a possibility.

The application of an overhead stirrer in a microwave-assisted pyrolysis reactor for oil pam shell biomass conversion was discussed by Salema and Ani [123]. In this research, the same microwave apparatus and temperature measurements as described previously [112] were used, with one modification made: using a three-necked glass lid at the top of the reactor instead of two-necked one in order to use an overhead stirrer. Oil palm shell biomass was used as the raw material and activated carbon was applied as the microwave absorbent. Four different ratios of biomass to activated carbon were used in this study: 1:01, 1:0.25, 1:0.5, and 1:0.75 (wt%). Nitrogen with a flow rate of 10 L/min was used for 5 min before starting the experiment and decreased to 5 L/min during the reaction to ensure an inert environment. Two different microwave exit powers of 300 W and 450 W in 25 min reaction time and constant stirrer speed of 200 rpm were the reaction conditions used for these experiments. The authors tested the oil palm shell without the activated carbon and it was found that no pyrolysis took place at input powers of 180 W and 450 W. The lowest amount of bio-oil yield was obtained when 10% activated carbon was applied, while the highest char yield was gained from the same amount of activated carbon. The biomass to activated carbon ratio was found to be a significant factor for reaction temperature and product yield. In addition, increasing the temperature to 900 °C increased the char yield significantly, while increasing the temperature from 400 °C to 700 °C decreased the char yield. In conclusion, it was observed that higher microwave pyrolysis temperatures can be achieved using mechanical stirrers, and that it enhances the heat transfer rate as well. Stirrers can also remove the hot spot phenomena in a multimode microwave. Time and energy were significantly reduced in terms of achieving complete pyrolysis and bio-oil quality was enhanced. However, the size and design of the stirrer had to be maintained to prevent interference from electromagnetic waves.

Aspen hardwood pellets were used as the raw material for catalytic microwave-assisted pyrolysis by Moen et al. [124]. A Sineo MAS-II batch microwave oven with 1000 W rated power was used at 800 W constant power, and chlorides, nitrates, metal-oxides and magnesium were added as the catalyst at 2% of the aspen mass (air dry aspen pellet weight basis) for the pyrolysis process. Chlorides, nitrates, and metal-oxides were found to favor the yield of liquid, pyrolysis gas, and heavy oil, respectively, while the light oil yield seemed to be constant. Chlorides increased the average liquid yield from 35% (without using catalyst) to 41% of the

total input biomass. The results indicated that the highest yield of gas (35.57%), char (32.01%), heavy oil (12.93%), and light oil (10.68%) were obtained using nitrates, without catalyst, metal-oxides, and chlorides, respectively. 69% and 18% of the total pyrolysis gas volume was found to be synthesis gas and methane, respectively.

Yu et al. [125] studied the microwave pyrolysis of corn stover (including stalks, leaves, cobs, and husks). The experiments were carried out in a microwave oven with input power ranging from 300 W to 900 W, and the reaction time did not exceed 60 min; a minimum power level of 300 W was required to initiate the pyrolysis process. The effect of adding charcoal (as the microwave absorbent) and NaOH (as the catalyst) were discussed in this study. The results indicated that increasing the microwave input power from 300 W to 900 W increased the gas and bio-oil yield while it decreased the charcoal yield. The maximum bio-oil and gas yield without using any additive was obtained at a microwave exit power of 900 W (30.2% and 46.9%), while the maximum charcoal yield was obtained for 300 W with 69.3%. The addition of 1 wt% charcoal showed significant increases in bio-oil and gas yield, while it had a negative effect on charcoal yield; for example, at 600 W, the addition of 1 wt% charcoal increased the bio-oil and gas yield from 25.1 wt% to 36.2 wt% to 29.5 wt% and 45.7 wt%, respectively. NaOH addition (5 wt%) to the pyrolysis process as the catalyst improved the gas yield greatly from 51 wt% to 57.5 wt% with an increase of input power from 300 W to 600 W.

Microwave pyrolysis was applied to oil palm fibers (as biomass solid waste) for bio-oil production by Salema and Ani [126]. A domestic microwave oven (1000 W rated power and 2.45 GHz frequency) was modified to accommodate the pyrolysis system. Char was added as the microwave absorbent to increase the heat transfer rate in this study at different proportions of 1:0, 1:0.25, 1:0.5, and 1:1 (biomass to char by weight of biomass). The microwave power was set at 450 W with the reaction time of 25 min, and nitrogen was purged with a flow rate of 20 L/min as the carrier gas. The maximum bio-oil and gas yield was recorded at (1:0.5) biomass to microwave absorber ratio, while the lowest char production was obtained using the same ratio. The result of this study showed that microwave pyrolysis can be applied to waste materials such as oil palm fiber for the production of bio-oil or any other value-added byproducts.

Palafox and Chase [127] evaluated the microwave-assisted pyrolysis process of high-density polyethylene and aluminum/polymer laminates in a semi-batch scale microwave reactor. The experiments were performed in a modified microwave oven with four magnetron of 5 kW maximum power output. Each magnetron can be controlled by separate switches and the microwave can generate continuous waves rather than on/off cycles. The reactor was equipped with a stirrer with the maximum speed of 6 rpm. The degradation of polyethylene pellets were carried out at different temperatures between 500 °C and 700 °C. The results indicated that the oil and gas yield could be kept relatively constant by changing the temperature in this study. The oil and gas yield was varied between 79.1 wt% and 20.9 wt% at 600 °C to 81.0 wt% and 19.0 wt% at 500 °C. In conclusion it was observed that the microwave pyrolysis process showed a great potential for problematic wastes such as toothpaste tubes.

Hanwu Lei et al. [128] investigated the effects of particle size (0.5–4 mm), reaction time (4–22 min), and temperature (515–685 °C) on microwave pyrolysis of corn stover for bio-oil, syngas, and biochar production. A batch microwave oven (Sineo MAS II, 1000 W rated power) was used at a power setting of 700 W and a 1 L quartz flask was placed inside the microwave. The used power gave the stage heating rates of 50 °C/min and 160 °C/min in the first 3 min and 3–5 min, respectively, and it reached the desired temperatures after 6 min. It was found that the maximum volatile yield of 76% (34% bio-oil and 42% biogas) could be obtained using 650 °C reaction temperature, and a particle size of 4 mm for 8 min. The size of particles was found to be insignificant for corn stover pyrolysis and these results indicated that microwave-assisted pyrolysis can be performed with large biomass materials. This means that there is no need for biomass grinding which is necessary in conventional pyrolysis.

Fernandez at al. [129] compared the effect of conventional and microwave-assisted methods for syngas production from glycerol on three different processes, namely pyrolysis, steam reforming, and dry reforming by using commercial activated carbon as the catalyst. The results proved that microwave-assisted heating method in all cases produced higher gas yields (converted from glycerol) with a large syngas content and a higher H_2/Co ratio in comparison with conventional heating methods. The lower yield of solid fraction such as CH_4, C_2H_4, and C_2H_6 was obtained by using a microwave irradiation heating system, which shows the potential of this method in decomposition reactions. Additionally, it was observed that the use of carbonaceous catalyst ameliorated the syngas production and produced the minimum amount of CO_2 emissions.

Xin-hui et al. [130] compared the preparation of activated carbon from *Jatropha hull* with two different conventional and microwave heating methods. A 3 kW, 2.45 GHz microwave oven and a quartz pipe located at the center of microwave were used to perform the experiments. The standard full factorial statistical response surface methodology (RSM) was applied to optimize the number of experiments. In this study, steam and CO_2 were used as activation agents for pyrolysis process. The observed results showed that microwave heating increased the production yield from 18.02% to 36.60% (double) using CO_2 as the activation agent, and that the activation temperature, activation time and CO_2 flow rate were clearly lower in comparison with conventional technique. This made the process more economical, although the porosity of carbon was in the same order of magnitude. It was also shown that the produced activated carbon yield did not appear to be affected much for steam activation using microwave or conventional heating methods, while the pore volume and the surface area was found to be double using a microwave-assisted heating system.

The effect of temperature and pyrolysis heating methods (conventional and microwave-assisted pyrolysis) on product yields and characteristics were studied by Dominguez et al. [49]. The coffee hulls were used as the raw material for pyrolysis process at 500 °C, 800 °C, and 1000 °C. It was observed that the amount of produced gas for this particular raw material was larger in comparison with other solid and liquid fractions even in low temperatures for both heating methods. Microwave heating methods could produce more gas and less oil in comparison with conventional methods. Additionally, the gas produced from the microwave heating method had higher H_2 and syngas contents (H_2+CO up to 40 vol% and 72 vol%, respectively) in comparison with conventional methods (up to 30 vol% and 53 vol%, respectively). The accumulated energy in gas and solid fractions increased and decreased with temperature respectively and the energy percentage accumulated in each fraction decreased as follows: gas > char > oil. The gas fraction yield in both methods was increased by temperature, while the solid fraction yield was decreased. The total yields of products were higher when using the microwave heating method.

The microwave-induced pyrolysis of glycerol using two types of activated carbon (obtained from bituminous carbon and coconut shell sources) for gas production was performed in a fixed-bed quartz reactor by Fernandez et al. [83]. A single-mode microwave oven and an electric furnace were compared to discuss the effect of the microwave heating technique. In this study, activated

carbon as the catalyst and microwave receptor resulted in a higher H_2 to CO ratio. The effect of heating methods (microwave irradiation and conventional) and reaction temperature (from 400 °C to 900 °C) were studied as well. The glycerol pyrolysis produced a high gas content up to 81 vol%. Microwave pyrolysis was proven to be a better method in comparison with the conventional method, even at low reaction temperatures like 400 °C. In addition, the results showed that the optimum reaction temperature for pyrolysis of glycerol was 800 °C and there was not much difference between the two different types of catalysts at this temperature. In addition, bituminous activated carbon proved to be more effective under the microwave technique and increased the amount of syngas produced.

Dominguez et al. [131] compared the bio-oil composition produced from microwave-assisted and conventional pyrolysis. Sewage sludge (three types from water treatment plants and one type from a milk-derivative factory) and graphite (between 0.5 g and 3 g) were used as the raw material and absorber (to increase the reaction temperature) for pyrolysis in this study, respectively. The pyrolysis of sewage sludge was performed in a 2.45 GHz multi-mode microwave oven using a quartz reactor. The results showed that the oil produced using a conventional electrical furnace at high temperatures was of considerable environmental concern, including compounds such as PAHs, while it had a high calorific value and a low proportion of PAHs when the microwave pyrolysis technique was applied.

Fernandez and Menéndez [132] studied the effect of initial characteristics of raw materials for syngas production under microwave and conventional heating, as well as their related time and energy savings. Microwave-assisted pyrolysis was applied to three different biomass wastes: sewage sludge, coffee hull, and glycerol. It was found that glycerol and sewage sludge yielded the highest and lowest syngas and the lowest and highest H_2/CO, respectively, while coffee hull yielded intermediate values for both. The microwave-assisted technique produced a higher gas yield with greater syngas content in comparison with the conventional heating method. In this method the pyrolysis temperature was increased because of the hot-spot phenomenon during microwave heating for all three raw materials. Additionally, the results demonstrated that the microwave heating method consumes less energy and time. Time savings ranged from 40% to 60% for different temperatures and raw materials and the energy consumption values were found to be lower than 0.004 kW h for microwave heating and higher than 0.005 kW h for the conventional method.

The influences of using graphite and char as absorbers and different types of microwave oven (multimode and single-mode) were studied by Dominguez et al. [133]. The wet sewage sludge was placed in a quartz reactor in the 2.45 GHz microwaves at 1000 W for drying, pyrolyzing, and gasifying processes. Pure graphite and char were used as microwave receptors to achieve the high temperatures required for the pyrolysis process. An electric furnace was used to compare microwave-assisted pyrolysis with conventional techniques. The microwave method was recognized as a rapid technique for pyrolysis and, although the absorbers were found to affect the quantity of oil produced, they did not have much of an effect on the quality of the oil. The multimode microwave oven ameliorated the dehydration and cracking processes in comparison to a single-mode oven. It was found that microwave-assisted pyrolysis required less processing time in comparison with an electric furnace.

Menendez et al. [134] investigated the microwave-assisted pyrolysis of four different types of wet sewage sludge from urban waste water treatment plants and milk-derivative factories. A lab-scale multimode microwave reactor was used for drying and pyrolysis of these waste materials. A quartz reactor was placed into a 2.45 GHz, 1000 W constant input power microwave oven and He was used as the carrier gas in the experiments. The results were compared with those from conventional pyrolysis methods and it was found that microwave pyrolysis required a much shorter time in comparison with an electrical furnace. Besides, microwave pyrolysis increased the syngas content (CO and H_2) of the produced gas up to 62% (means a lower production of non-condensable gases) which it is about 25% of the levels produced by conventional heating.

The effects of microwave irradiation and conventional heating on the pyrolysis of CH_4 over activated carbon (as a microwave absorber and catalyst) were analyzed by Fidalgo et al. [135]. In this work, the influence of applying different ratios of CH_4 to N_2 for production of H_2 from methane was also studied. A quartz reactor was used in both an electric furnace (EF) (conventional heating) and a single-mode microwave oven (MW) to perform the experiments at 800 °C for 65 min. In this study, N_2 improved the conversion yield significantly, although it seemed to have different effects depending on the heating source; it enhanced the pyrolysis only by distributing the methane molecules within the activated carbon bed when EF was the heating source, while it had another significant effect of energetic microplasmas generation (resulting in higher conversions) when the MW was applied, as well as distributing the CH_4 molecules when MW was the heating source.

Sewage sludge was used as the raw material for microwave-assisted drying, pyrolysis and gasification (MWDPG) by Menendez et al. [136]. The authors aimed to reduce the volume of initial sludge and solid residue by using this method. A single-mode microwave oven (2.45 GHz with maximum delivered power of 2 kW) was used for MWDPG process of sewage sludge. The exit power was set at 1000 W at the beginning of the experiment to reach the desired temperature (1000 °C) and after that it was set at 600 W for the rest of the experiment; the microwave irradiation time was about 15 min. Helium was applied as the carrier gas with the flow rate of 100 mL/min. All of the experiments were repeated in an electric furnace in order to compare the results with the microwave irradiation method. The microwave-assisted process improved the CO and H_2 contents of the gas and reduce the PAH content in the produced oil, while it had little influence on the solid fraction yield in comparison to the conventional method and only slightly reduced the solid residue yield. However, it was found to produce a very low volume of solid residue.

Wang et al. [137] investigated the microwave-induced torrefaction (mild pyrolysis) of rice husk and sugarcane residues. In this study, the effects of processing time, water content, particle size, and microwave power level were explored. A single-mode microwave oven (2000 W and 2.45 GHz) was used to perform the torrefaction. Nitrogen (N_2) was applied as the carrier gas with a flow rate of 50 mL/min. The proper microwave exit power was between 250 W and 300 W. It was observed that this method can ameliorate the calorific value of sugarcane residue and rice husk by 57% and 26%, respectively, and that the biomass particle sizes in microwave-assisted torrefaction do not need to be very small. It can also increase the carbon content and decrease the oxygen content of the solid fraction in comparison with other conventional methods.

Domingues et al. [138] investigated the microwave-assisted pyrolysis of sewage sludge for bio-fuel preparation and more specifically to maximize the gas yield and to improve the quality as a source of hydrogen and syngas (H_2+CO). The experiments were carried out using both single-mode and multimode microwave cavities (constant 1000 W input power) using the reactor. All of the experiments were repeated in an electrical oven as the heating source to study the actual effects of the microwave irradiation technique. Graphite and char were applied as the microwave absorbers to increase the heating intensity and He

was used as the carrier gas with a flow rate of 100 mL/min. It was concluded that microwave irradiation improved the proportion of gases produced (up to 38% for H_2 and 66% for H_2+CO) in comparison with the applied conventional method. Additionally, it was observed that microwave irradiation improved the char production and decreased the reaction time from 24 min to 10 min. Single-mode was recognized as a better heating source for gas production, while multimode was a better option for char production.

Waste polystyrene was converted to useful hydrocarbon by using microwave pyrolysis reaction (interaction of microwave with aluminum in the form of coiled wire, strips, and cylinder) at the melting point temperature of aluminum by Hussain et al. [139]. A domestic on/off microwave oven (medium size with 2.45 GHz frequency) was modified for these experiments. A baked clay cylindrical reactor was placed in a microwave for microwave pyrolysis. The waste materials were converted to an aromatic oil/ liquid (88 wt%), olefinic and paraffinic gasses (9–10 wt%), and a solid char-like residue (the rest). The reaction was found to be faster for the coil, slower for the strips, and negligible for the cylindrical form. Microwave heating was found to be an effective alternative method in comparison to conventional heating to reduce the reaction time and consequently cost, and improve the quantities of liquid products.

Microwave-assisted pyrolysis was applied to large pieces of larch, namely lumber (cylindrical block samples with 60 mm diameter and 60 mm height) and cellulose fiber paper by Miura et al. [140]. The samples were placed in the modified household microwave oven (2.45 GHz and 600 W) for a short irradiation time. The char residue was about 39 wt% and 35 wt% with 6 min and 8 min reaction times, respectively, while the yield of tar was relatively constant (about 20 wt%). It was also found that the char residue and tar yields were 47.3 wt% and 18.6 wt%, respectively, with a 7 min reaction time. In this study, it was proven that dielectric heating reduces the pyrolysis time significantly and improves the surface area of produced char in comparison with conventional heating techniques.

Rapid pyrolysis of cylindrical wood blocks by microwave heating was discussed by Miura et al. [141]. Two types of microwave ovens of 1.5 kW and 3 kW were used as heating apparatus for pyrolysis of wood blocks with 60–300 mm diameter and 80–12,000 g weight. One of the microwaves was a relatively small-scale oven (1.5 kW) designed for pyrolysis of small wood samples, while the other (3 kW) had a bigger reaction chamber. In this study, it was found that microwave irradiation increased the temperature in the center of the wood rather than the surface in the outer region. The results showed that when the char yield was about 20% its specific surface area was about 450 m^2/g which is around 2.5 times that produced by conventional heating (184 m^2/g). Additionally, it was observed that larger wood blocks can be pyrolyzed with less electric power consumption per unit weight than smaller wood blocks. The yields of produced tar in this research were about 15–30 wt%.

This review paper identifies several issues and challenges related to microwave pyrolysis. Accurate measurement of temperature is one of the most important challenges under microwave pyrolysis as it affects the reaction conditions and efficiency. Choosing a proper temperature sensor seems critical to reduce measurement errors. From the above literature, it was found that most of researchers used contact type sensors like grounded thermocouple probes. The advantages of using these types of thermocouple probes are; first it is normally metallic shielded type of thermocouple and does not react with the media itself. Second, it is directly in contact with the biomass, so the temperature is the temperature of the reaction mixture. Third, response time of the grounded thermocouple probes is quicker than the ungrounded ones because the sensing junction is wired directly to the probes wall. The disadvantage of grounded thermocouple probes is that sometimes it has interaction with electromagnetic fields, thus the readings will not be that accurate. Infrared optical pyrometers can be used in combination with grounded probe thermocouples as an attempt to solve this problem and improve the reliability of temperature monitoring system.

On the other hand, most of microwave pyrolysis units summarized in this paper have the power control system (with on-off switching system). However, one of the important tools to reach a consistent pyrolysis reaction condition is having a temperature-feedback control system. Stabilizing the reaction conditions provide less retention time and solidity in produced bio-products.

Another challenge in microwave pyrolysis is that until today all the researchers have investigated the feasibility of this process at lab scale basis. Only small quantities of original biomass, residues or wastes (3–400 g) are pyrolyzed in the system to test the feasibility. None investigated this process at pilot scale, while it needs scaling up for commercialization.

Finally, as pyrolysis is known as one of the best methods to recover the energy and chemical value of residues and wastes, a continuous microwave pyrolysis system can be a solution to many problems faced by other methods.

5. Variables affecting the microwave-assisted pyrolysis process

The yield and quality of produced value-added products are affected by some critical parameters in the microwave-assisted pyrolysis process. In order to obtain the highest quality and maximum conversion yield, these variables should be optimized. The most important variables in microwave-assisted pyrolysis reaction processes are listed below:

- Type and size of input biomass/materials
- Moisture and water content of input biomass/materials
- Reaction temperature
- Reaction time (residence time)
- Microwave output power
- Microwave type (multimode or single-mode)
- Reactor design/type
- Microwave receptor type, size, and amount/concentration
- Catalyst type and concentration
- Mixing intensity (stirring)
- Type and flow rate of carrier gas

6. Advantages of microwave-assisted pyrolysis technology

Microwave-assisted pyrolysis technology has the potential for energy and cost reduction. It has been proven as a powerful tool in waste reduction, material recovery, and converting biomass and bio wastes into value-added products. However, this method has not been industrialized yet, although it is an attractive option for further industrialization. In this section, the advantages of microwave-assisted pyrolysis technology are summarized as an efficient alternative method to conventional technology.

Fast, selective and uniform heating are the first advantages of this method, which make the treatment and utilization of non-homogeneous wastes and large size biomass possible. Thus, the solid feedstocks with high moisture content, including forest and agricultural wastes and residues, municipal solid wastes (MSW), and municipal waste solid sludge, can be treated using this method. It enhances the product quality, chemical reactions, and overall efficiency. Process flexibility and equipment portability are the other advantages of this technique.

The World Commission on Environment and Development was set up by the United Nations and was headed by Gro Harlem Brundtland to find solutions for the sustainability of human activities. The outcome of this study has become a guideline for sustainable development and was published as a book entitled "Our Common Future" [142]. Sustainable development was defined as meeting the requirements of the present generation without compromising the needs for future generations [143]. Thus, in order to fulfill these aims and standards, the interest in the production of bio-products, such as bio-oil, biochar, and syngas, has been stimulated globally. Microwave-assisted pyrolysis can be a pathway out of poverty for developing counties. Moreover, it can provide new incentives for agricultural research and development investment, offer farmers a source of income, help in carbon sequestration, increase crop and land yield and productivity, improve sustainable land use in agriculture, and provide new incentives for municipal solid waste (MSW) and sludge treatment research and development as well [144].

7. Future directions

Considerable attention has been given to renewable substitutes for fossil fuels due to the twin problems of fossil fuel depletion and environmental degradation, increasing the population, and tremendous amount of wastes. Both thermochemical and biochemical processes can be applied to upgrade the biomass. Pyrolysis is a thermochemical method of energy recovery from biomass resources and offers higher energy production efficiency and less pollution. It allows higher energy recovery from biomass materials, especially wastes, and it can be applied as either primary processing (in incineration or gasification) or independent processing leading to the generation of a variety of different products. Therefore, it can be an alternative for amelioration of energy security and emission reduction. This method has gained a great deal of attention and its future is growing, yet it is still under development. The cost of final products depends on many factors including the feedstock availability/cost and production technology cost. The cost of the pyrolysis process is the main aspect associated with the processing cost. Thus, improving the pyrolysis technology is one of the options for reducing the cost of products. Microwave technology is a well-established method which can be applied to thermochemical processes such as pyrolysis for energy and consequently cost reduction. The microwave-assisted pyrolysis technique offers some unique advantages, like time and energy savings, which cannot be attained with other conventional heating methods. Generally, in this method, feedstock properties and reaction conditions are two effectual elements influencing the pyrolysis characterization and yield of final products. There are few main limitations which strongly affect the industrialization of this technique. The absence of sufficient data to quantify the dielectric properties of input feedstocks to design and develop a microwave-assisted pyrolysis conversion unit, doubts about the actual cost of the technique, and the heat, mass transfer, and chemical reactivity nature of the microwave heating method are some of these limitations. These concepts can be studied in future researches to develop a more economic microwave-assisted pyrolysis unit. Finally, the creation of a dependable bioenergy production chain, industry acceptance, cost reduction, and processing technology maturity are vital factors which can help policy makers and pyrolysis industry players establish a more sustainable pyrolysis market in the long-term.

8. Conclusions

In conclusion, pyrolysis is one of the most important bioconversion routes to convert biomass virgin resources, biomass residues and wastes (non-conventional sources), and municipal solid wastes and sewage sludge into value-added products. It involves the well-established thermochemical decomposition of biomass (hydrocarbon or organic materials) at elevated temperatures in the absence of oxygen, and can provide a variety of energy-dense products in three different phases: solid, liquid, and gas. All of these pyrolysis products, including carbonaceous residue (char/biochar), bio-oil, and syngas, are potential substitutes for the currently available fossil fuel based energy resources. The adoption of these fuels has some principal advantages, such as natural energy resource security improvement, emission and pollution reduction, and it can be a suitable pathway for sustainable development. Apart from these, it also has some other advantages, especially with regard to the economic development of rural communities: it can be one of the easiest ways to adapt to current energy infrastructure and deal with the tremendous amount of waste produced in the world. The conventional heating method is one of the traditional techniques applied to pyrolysis, although other emerging technologies such as microwave-assisted techniques have been recently introduced. The microwave-assisted pyrolysis technique is reviewed in this paper as an attempt to find a way to reduce the production cost whilst increasing the quality of products. It was observed that this technique is a well-established pathway that can be enhanced to accelerate the pyrolysis process in comparison to conventional techniques. Additionally, variables affecting the microwave-assisted pyrolysis technique and advantages of this method are summarized in this paper. It was concluded that the microwave-assisted pyrolysis technique can provide selective and rapid heating, is a way to reduce the waste volume and can also be used to treat the waste in situ. In addition, it is a cleaner process in comparison to conventional techniques, which can enhance chemical reactivity, save the required processing energy, and consequently reduce cost.

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